

ADSORPTION OF SO₂ ON BITUMINOUS COAL CHAR AND ACTIVATED CARBON FIBER PREPARED FROM PHENOL FORMALDEHYDE

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INTRODUCTION

Carbon-based materials are used commercially to remove SO₂ from coal combustion flue gases. Historically, these materials have consisted of granular activated carbons prepared from lignite or bituminous coals [1-3]. Recent studies have reported that activated carbon fibers (ACFs) may have potential in this application due to their relatively high SO₂ adsorption capacity [4-6]. In this paper, a comparison of SO₂ adsorption for both coal-based carbons and ACFs is presented, as well as ideas on carbon properties that may influence SO₂ adsorption.

EXPERIMENTAL

Sample Preparation

The chars used in this work were prepared from an Illinois No. 2 hvCb coal, sample IBC-102 of the Illinois Basin Coal Sample Program [7]. A physically cleaned 48x100 mesh sample having 3.6% mineral content was prepared from the parent coal and used throughout as the feedstock for activated char. Chars were prepared at 900°C for 0.5 h in a 5 cm ID batch fluidized-bed reactor (FBR). In each run, 200 g IBC-102 coal was fluidized in flowing N₂ (6 L/min) and heated to the desired pyrolysis temperature. A multistep heating procedure was used to minimize agglomeration of coal particles in the FBR. Steam activation was done to develop microporosity and increase surface area further. Typically, 50 g of char was placed in the FBR and heated to 860°C in flowing N₂. The N₂ flow was replaced by 50% H₂O/50% N₂ (6 L/min) for 0.75 h to achieve 30% carbon conversion. In some cases, the H₂O-activated char was treated with nitric acid (HNO₃). Typically, 10 g of the char was added to 0.2 L 10 M HNO₃ solution, and refluxed at 80°C for 1 h. The HNO₃-treated carbon was washed with distilled H₂O to remove excess acid and vacuum dried overnight at 25°C. In some cases, the HNO₃-treated char was heated in N₂ to 525, 725, or 925°C and held for 1 h to remove oxygen placed on the carbon by the HNO₃ treatment.

ACFs with surface areas and oxygen contents ranging from 700 to 2800 m²/g and 0 to 5 wt%, respectively, were prepared commercially by reacting phenol formaldehyde fiber precursors (Kynol) in a steam/carbon dioxide mixture at temperatures between 700 and 900°C. ACFs with acidic and basic surface chemistry were prepared using methods described elsewhere [8,9].

Sample Characterization

The SO₂ adsorption capacities of samples were determined by thermogravimetric analysis (Cahn TG-131). In a typical run, a 30-50 mg sample was placed in a platinum pan and heated at 20°C/min in flowing N₂ to 360°C to remove moisture and impurities. The sample was cooled to 120°C. Once the temperature stabilized, the N₂ was replaced by a mixture of gases containing 5% O₂, 7% H₂O and the balance N₂. Once there was no further weight gain due to adsorption of O₂ and H₂O, SO₂ was added in concentrations representative of a typical flue gas from combustion of high sulfur coal (2500 ppmv SO₂). The weight gain was recorded versus time by a computerized data acquisition system.

Temperature programmed desorption (TPD) experiments were done in a flow-thru, 2.5 cm ID stainless steel fixed-bed reactor system. In a typical run, 0.5 g of sample was heated in flowing nitrogen (0.5 L/min) at 5°C/min to a final temperature of 1000°C and held for 1 h to achieve nearly complete desorption of CO and CO₂ from the carbon surface. Non-dispersive infrared analyzers (Rosemount Model 880) were used to monitor the concentrations of CO and CO₂ in the effluent gas continuously.

N₂ BET surface areas of chars were determined using a single point BET adsorption equation with N₂ (77 K) adsorption data obtained at a relative pressure (P/P₀) of 0.30 with a Monosorb flow apparatus (Quantachrome Corporation). Surface areas were determined for ACFs with a Micromeritics analyzer using nitrogen adsorption at 77K. Average pore sizes of ACFs were calculated using the Dubinin-Radushkevich equation and the nitrogen adsorption isotherm measured using a Coulter Omnisorb.

RESULTS AND DISCUSSION

Coal Chars

The results presented in Figure 1 suggest a lack of correlation between SO₂ adsorption and N₂ BET surface area. Two steam activated carbons prepared from IBC-102 with intermediate surface areas (200 and 360

m²/g) and a commercial activated carbon, Calgon F400 (1000 m²/g), adsorbed similar amounts of SO₂ (between 15 and 20 wt% SO₂) after about 4 hours. The Centaur carbon, which had the highest SO₂ adsorption capacity, had an N₂ BET surface area of only 360 m²/g. This carbon catalyst was developed by Calgon for both liquid and vapor phase applications, including removal of SO₂ and NO_x from flue gas. Figure 1 also shows that an activated carbon prepared from IBC-102 coal by steam activation, HNO₃-treatment and subsequent heat treatment to 925°C exhibited SO₂ adsorption behavior similar to the Centaur carbon. One study [10] showed that there was no correlation between the SO₂ adsorption capacity and surface area of a coal-based carbon, while another [11] has maintained that "surface area is the most important parameter in order to predict the behavior of a char in the abatement of SO₂ from exhaust gases."

A better understanding of SO₂ adsorption behavior may require more detailed information about the carbon-oxygen (C-O) complexes formed during char preparation and SO₂ adsorption. The authors showed previously a poor correlation between SO₂ adsorption capacity and the total amount of chemisorbed oxygen for chars prepared under a wide range of conditions [12-14]. Davini [15] also observed no correlation between SO₂ adsorption and chemisorbed oxygen. He found a better correlation between SO₂ capacity and the basic (or high temperature) C-O functional groups. In the current study, the steam activated char was found to have a surface populated predominantly by high temperature C-O complexes. To increase the number of high temperature C-O complexes, and presumably SO₂ capacity, the H₂O-activated char was treated with HNO₃ and thermally desorbed at temperatures ranging from 200 to 1075°C. Figure 2 presents the TPD profiles of the HNO₃-treated char and those thermally desorbed at 525, 725 and 925°C. The CO and CO₂ evolution profiles of the original HNO₃-treated char showed only slight overlap. Conceivably, this char could be heated in inert gas to a certain temperature, e.g., 525°C, to remove only the CO₂-forming functional groups and retain the CO-forming ones. Figure 3 shows that the SO₂ adsorbed increased with increasing thermal desorption treatment. A three-fold increase in SO₂ adsorption is observed with the relatively small increase in thermal desorption temperature from 525 to 725°C, and the char with the smallest amount of C-O complex (925°C) adsorbed the largest amount of SO₂. This suggests that sites that form a stable C-O complex during char preparation are made available by the thermal desorption treatment, and that adsorption of SO₂ may preferentially occur at these free adsorption sites. Using TPD, the authors previously measured the number of free adsorption sites for several carbons; a direct relationship was found between SO₂ capacity and free sites [12,14,16]. Based on these results, a reaction scheme was recently proposed to explain SO₂ removal by carbon whereby the free sites control the rate of adsorption of SO₂ and conversion to H₂SO₄ [17,18].

ACFs

Figure 4 shows that the SO₂ adsorbed varies inversely with surface area for the ACFs studied. The pore volumes of these ACFs are known to increase from about 0.3 (ACF-10) to 0.8 cm³/g (ACF-25) [19]. Others have also observed a decrease in adsorption of SO₂ with increasing surface area and micropore volume of ACF (polyacrylonitrile fibers) [4,6]. The oxygen and nitrogen (< 0.05%) content, although not measured directly for this series of ACF, should not have varied much among these four samples; although, the oxygen content of ACF-10 and 15 may have been slightly greater than that of ACF-20 and 25 [19,20]. Excluding the idea of free sites for now, the results presented in Figure 4 suggest that pore size was the most important factor for determining the SO₂ adsorption properties of these ACFs. These ACFs are known to have relatively narrow pore size distributions [20,21]. In this study, we calculated the average pore sizes of ACFs 10, 15, 20 and 25 to be 9.4 Å, 11.7 Å, 13 Å and 17.5 Å, respectively. Foster et al. [19] studied a series of ACF similar to those used in this study and found that for ppm levels of n-butane, benzene or acetone, low surface area ACF adsorbed more than high surface area ACF. It is well known that smaller pores are preferentially filled at low relative pressures (concentrations) of adsorbate due to the overlap of attractive forces of opposite pore walls. If a similar adsorption mechanism occurs in the SO₂-ACF system as in the n-butane-ACF system, this would explain the behavior observed in Figure 4, and help explain the lack of correlation between N₂ BET surface area and SO₂ capacity observed for the coal chars. Ultimately, the number of free sites as well as pore size distribution and pore volume of an activated carbon should define its SO₂ adsorption behavior. The relative importance of each remains to be determined.

Figure 5 shows that the ACF-10 treated with both sulfuric and nitric acids (H₂SO₄/HNO₃) and thermally desorbed to 400 and 700°C exhibits SO₂ adsorption behavior similar to that of the HNO₃-treated, thermally desorbed coal chars (Figure 3). The SO₂ adsorption capacity of the H₂SO₄/HNO₃ treated carbon thermally desorbed at 700°C is much greater than that of the original ACF-10. The presence of adsorbed O₂ on ACF may serve only to block access of SO₂ to free active sites, similar to the behavior we have observed for Illinois coal char. Heating the H₂SO₄/HNO₃-treated ACF to 700°C would gasify part of the ACF, evolving oxygen as CO or CO₂, thus increasing the average pore size. If the average pore size of ACF increases with oxidation/thermal desorption, the results shown in Figure 4 would predict a decrease in the SO₂ capacity of H₂SO₄/HNO₃ treated ACF thermally desorbed at 700°C, if pore size was the only controlling factor. The fact that there was an increase in SO₂ adsorption despite an increase in pore size suggests the strong influence of free sites in controlling SO₂ adsorption behavior. It remains to be determined whether the free site concentration of these ACFs can be measured. It is interesting that the thermal desorption treatment applied to both the H₂SO₄/HNO₃-treated ACF and the HNO₃-treated coal char serves to increase not only the SO₂ adsorbed, but also the initial rate of SO₂ adsorption (Figures 3 and 5); this behavior has been attributed to an increase in the number of active sites [22].

Modifying the surface chemistry of ACFs by incorporating different functional groups has been shown to improve adsorption of various adsorbates [8,9,19,20,23,24]. ACFs with both acidic and basic surfaces, and an average pore size smaller than the original ACF-10, were prepared using methods described in previous work [8,9]. Since SO_2 is an acid gas, a carbon with basic surface characteristics would be expected to exhibit enhanced SO_2 adsorption. Indeed, Figure 6 shows that a basic ACF adsorbs more SO_2 than an acidic ACF. Others have also suggested that the presence of small amounts of nitrogen in ACF can markedly improve its SO_2 removal capabilities [4,6,25,26]. Work is in progress to learn how the interrelationships among number of free sites, pore size distribution and types of functional groups may control a carbon's SO_2 adsorption behavior [27].

CONCLUSIONS

Coal-based activated carbons and ACFs, prepared by a novel oxidation/thermal desorption treatment, had SO_2 adsorption capacities approaching that of a commercial carbon catalyst. The current price of ACFs, about \$10/lb., may limit their use in SO_2 removal applications, however, some recent work suggests that ACFs can be prepared for \$1- \$2/lb. [28]. Further work is needed to characterize these less expensive ACF systems for SO_2 removal. The results obtained in this study suggest that pore size as well as the number of free active sites play important roles in determining a carbon's SO_2 adsorption capacity. The complete pore size distributions of the treated coal-based carbons and ACFs remain to be determined; these should provide additional insight into the relative importance of pore size and free sites in controlling SO_2 adsorption behavior. The use of functional groups, e.g., nitrogen-containing ones, to modify a carbon's surface to improve SO_2 adsorption appears promising, and is also an area for further investigation.

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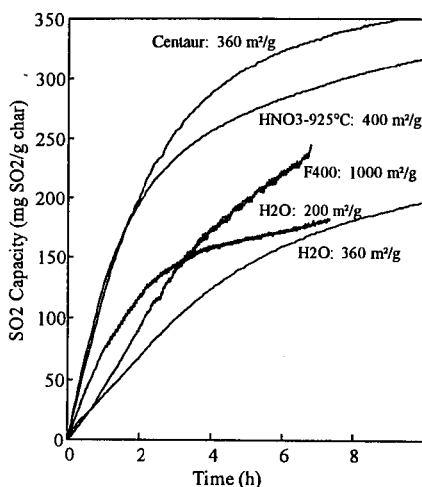


Figure 1. Effect of N₂ BET surface area on SO₂ adsorption capacity of selected IBC-102 chars and commercial carbons.

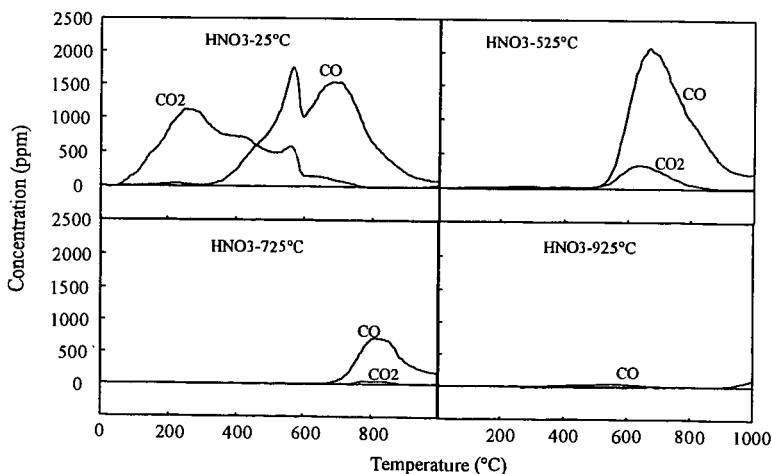


Figure 2. TPD profiles of nitric acid treated/thermally desorbed IBC-102 chars.

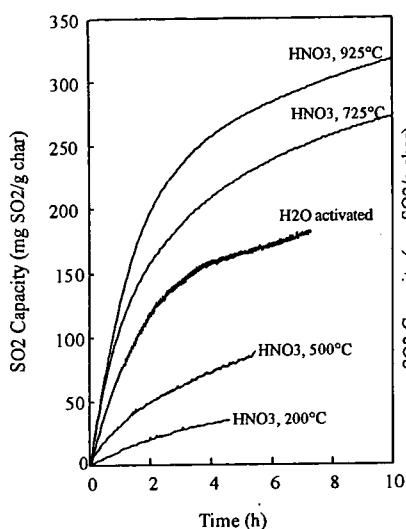


Figure 3. SO₂ adsorption for HNO₃-treated chars desorbed to different temperatures.

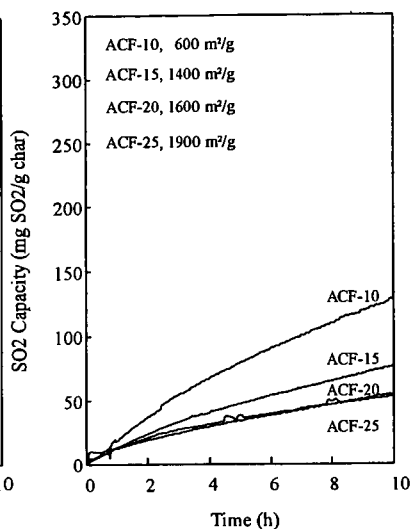


Figure 4. SO₂ adsorption for ACFs.

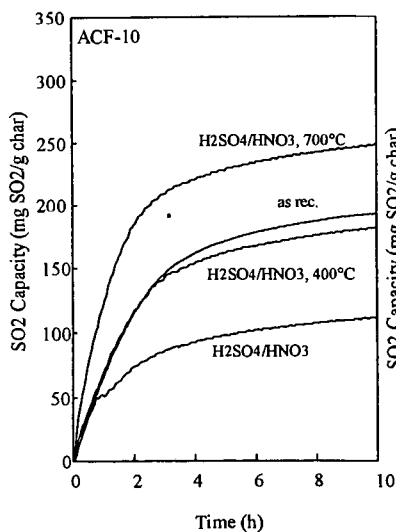


Figure 5. SO₂ adsorption for oxidized ACFs desorbed to different temperatures.

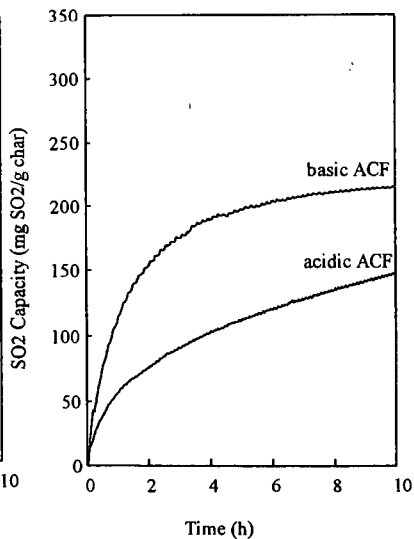


Figure 6. SO₂ adsorption for acidic and basic ACF.